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TITLE	(54):	METHOD FOR THE MANUFACTURE OF POLYVALENT ISOCYANATES
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### **Method for the Manufacture of Polyvalent Isocyanates**

This present invention concerns a method for the manufacture of diphenyl methane diisocyanate-containing polymethylene polyphenyl isocyanates which are suitable for use as a wood glue by way of the condensation of formaldehyde and aniline and phosgenation of the reaction product.

As is known from prior art, a mixture of diphenyl methane diisocyanate and polymethylene polyphenyl isocyanates is obtained through the phosgenation of a diamine and/or polyamine intermediate product that is obtained through the condensation of aromatic amines and formaldehyde in the presence of mineral acids.

These polyisocyanates play an important role in the manufacture of polyurethane hard foams. However, they are also suitable for use as glues in the manufacture of plywood and, in particular, particle boards.

The polyisocyanates used in the production of foams are subject to the highest requirements in terms of composition and purity to obtain the desired foam quality during the very sensitive foaming process. To meet these quality requirements, for the manufacture of suitable polyisocyanate mixtures, a number of different measures are required: already during the manufacture of the polyamine intermediate product, strict quantity limits must be maintained for both the initial and auxiliary substances to obtain the required isomeric and oligomeric ratio that is required for foam production. In addition, several cleaning steps are performed to meet the quality requirements.

All technical methods known from prior art therefore produce polyisocyanates in a manner that is too complicated to use them in an economical manner as a glue for particle boards, which are subject to less stringent quality requirements.

The object of this present invention is therefore to provide a simplified method for the manufacture of diisocyanates and/or polyisocyanates by way of phosgenation of the diamine and polyamine intermediate products that are obtained through the condensation of formaldehyde and aniline with acidic catalysts, which is simple, environmentally friendly and produces little waste and provided polyisocyanates which are particularly suited as wood glues.

It has been found that this object is achieved in that,

- a) during a first step, aniline and aqueous formaldehyde are condensed in the presence of hydrochloric acid, [and] the reaction mixture is distilled without neutralization while separating and optionally recycling water and/or non-converted aniline, and
- b) during a second step, the non-neutralized polyamine/polyamine hydrochloride mixture that was obtained during the first step is transferred in liquid hydrogen chloride as a suspension means to polyamine hydrochloride and, while adding liquid phosgene, the hydrochloride is converted to the polyisocyanate.

In the first step of the method hereof, it is particularly important that no neutralization of the hydrochloric acid that is used as a catalyst takes place and that the polyamines are not isolated as free bases, but occur in the form of a mixture of a free base and amine hydrochloride.

Considering that, at temperatures of less than 120° C, only the polyamines represent more or less viscous liquids, while the hydrochlorides, however, are salt-like solid products, it is advantageous to select the quantity of hydrochloric acid in such a manner that the polyamine/polyamine hydrochloride mixture that is formed has a melting point of less than 120° C. In case the mixture melts above 120° C and remains under these conditions for a more prolonged period of time, it is possible that the free primary amino groups are converted to undesired successor products in the presence of amine hydrochlorides.

The fact that the polyamine/polyamine hydrochloride mixtures are molten facilitates both the distillative separation of water and excessive aniline as well as the technical handling of the subsequent phosgenation.

To obtain such intermediate products, which are preferably meltable below 120° C, the molar ratio between aniline and hydrochloric acid during the first step should be between 15 to 1 and between 160 to 1; most preferably, however, it is between 20 to 1 and 80 to 1.

The properties, in particular the viscosity, of the polyisocyanate which is formed as the final product are particularly influenced by the molar ratio between aniline and formaldehyde. Depending on the desired properties, the molar ratio can be adjusted between 4.0 to 1 and 1.5 to 1, preferably between 1.8 to 1 and 2.5 to 1. The hydrochloric acid that is used as a catalyst during the first step of the reaction may be used as aqueous solutions or also in gaseous form. As gaseous hydrogen chloride, it is advantageous to use a part of the hydrogen chloride that is released during the phosgenation step.

Initially, the reaction between aniline and formaldehyde in the presence of hydrochloric acid is preferably performed at temperatures of between 20 and 50° C. It is advisable to increase this temperature, as soon as the Schiff bases have formed, to between 80 and 150° C, preferably to between 100 and 120° C, considering that for practical purposes, the reaction is not complete below 80° C. The reaction temperature may change step-by-step or continuously from the low to the high temperature range and can be changed quickly or slowly.

Continuously, the reaction is preferably performed in a cascade of stirrer vessels with two or more stirrer vessels.

A reaction tube divided into properly temperature-controlled sections may also be used .

The reaction time is approx. two hours or more; preferably, however, is ranges from four to six hours.

The raw product obtained in such a manner can be separated during a single-step distillation process from water and excessive aniline at a maximum sump temperature of 120° C (1 mbar). In the case of a two-step distillation process, separation can be achieved in an even less invasive manner, considering that shorter residence times are required. In the process, during a first step, water and aniline are removed up to a residual content of approx. 20%, and the remaining water and aniline are removed during a second step, within the scope of a thin-film distillation process at 150° C and 5 torr, using a residence time of between one and three minutes. The aniline that is recovered can be recycled.

The polyamine/polyamine hydrochloride mixture obtained in such manner is converted, during the second step of the method in accordance with this present invention, into a polyisocyanate mixture. First, the remaining free amino groups are transferred to hydrochlorides, and the polyamine hydrochloride mixture obtained in such a manner is converted to the polyisocyanate by using phosgene.

For that purpose, in a first reaction zone, the molten polyamine/polyamine hydrochloride intermediate product is added to liquefied hydrogen chloride, and the solid precipitation that is instantly formed is optionally reduced by using a grinding device until there are no more free amino groups. To the suspension of amine hydrochloride in liquid hydrogen chloride that is formed in such a manner, the phosgene is added in liquid form in order to convert it to the isocyanate, and the mash is transferred to another reaction zone were, at a high temperature [and] a pressure that is sufficient to maintain the excessive phosgene in a liquid phase, the amine hydrochloride is converted to the desired organic isocyanate and water-free hydrogen chloride, which is continuously removed from the reaction mixture.

The first reaction step is performed e.g. at normal pressure with hydrogen chloride that was liquefied by cooling it to below its boiling point. In a more advantageous manner, however, hydrochloride formation is achieved at a pressure of between 10 and 60 bar and a temperature of between -30 and +40° C. In a particularly preferred manner, the pressure used for the conversion with phosgene or a slightly higher pressure are applied.

Quick crushing of the solid mixture supplied as a molten material composed of polyamine and polyamine hydrochloride to the smallest possible particle size is preferably performed in a grinding device at an energy density of more than 5 kW/m<sup>3</sup> of grinding volume, wherein the solid is reduced to an average particle size of between 1 and 100µ. The size reduction is continue until quantitative conversion of the free amino groups to amine hydrochlorides is achieved.

The residence times largely depend on the efficiency of the grinding device used and may range from 1 second to 7 hours, preferably from 10 seconds to 50 minutes. The amine hydrochloride content of the suspension that forms can be varied over a wide range, although preferably, it is maintained in the range between 5 and 25 percent by weight.

In case a grinding pump with circuit-based transportation of the hydrochloride HCl suspension is used, this step can be performed continuously. Several such grinding circuits can also be disposed successively.

Afterwards, between two and five times the molar excess of liquid phosgene is added to the suspension of amine hydrochloride and hydrogen chloride, and the suspension is transferred to the second reaction zone.

There, in a heated pressure vessel, at a temperature of between 100 and 180° C, the amine hydrochloride is further converted by using phosgene to form carbamyl chloride and decomposed to isocyanate and hydrogen chloride. To obtain a liquid phosgene phase, the reaction pressure is kept between 15 and 55 at. The hydrogen chloride is condensed in a cooler and, as a reflux, transferred to a mounted column in such a manner that, on the cooler head, pure hydrogen chloride can be removed for recycling to the manufacture of bases as well as for the production of hydrochloride.

Upon completion of HCl separation, the resulting polymethylene polyphenyl polyisocyanate and excessive phosgene remain in the reactor, which can be separated and recovered for reuse.

The quantitative data specified in the following examples represent parts by weight. The ratio between parts by weight and parts by volume is identical to the ratio between kilogram and liters.

### **Example 1**

To a mixture of 391 parts of aniline and 20 parts of 56% hydrochloric acid, while stirring, 200 parts of a 30% aqueous solution of formaldehyde are added within 50 minutes in such a manner that the temperature does not exceed 50° C. From the reaction mixture that is drawn off, afterwards, at normal pressure, water is removed through distillation until the sump temperature has reached 120° C. In the process, azeotropically converted aniline is recycled to the reaction mixture. After a residence time of two hours at 120° C, the conversion is completed.

Subsequently, the reaction mixture is freed, at 150° C and 5 torr in a thin-layer evaporator (Sambay system), from residual water traces and unconverted aniline. From the polyamine/polyamine hydrochloride mixture that has formed, 60 parts are added as a molten material at 100° C to 400 parts of hydrogen chloride at a temperature of -100° C. To ensure proper mixing of the suspension and size reduction of the formed solid, the reaction mixture is stirred by using a turbomixer (Turrax system, TV 45). After mixing for 30 minutes, the main quantity of hydrogen chloride is removed through distillation, and 400 parts of liquid phosgene are added. The reaction mixture which has been heated to 0° C is then transferred into an autoclave with a capacity for 600 parts by volume with a mounted cooler. The autoclave is

heated to 150° C and, through expansion of the hydrogen chloride on the head of the cooler that is used for phosgene condensation, kept at 33 to 35 of gage pressure. Once the formation of hydrogen chloride has been completed, autoclave pressure is relieved, as a result of which the excessive phosgene is removed through distillation. The resulting isocyanate mixture is freed from any phosgene residues under a vacuum of 5 torr at 160° C within 5 hours. The 66 parts of polyisocyanate mixture that are obtained have a viscosity of 166 cSt at 25° C and a content of NCO groups of 31.5 %.

### **Example 2**

To produce an amine/amine hydrochloride mixture, to 335 parts of aniline, 100 parts of 1 molar aqueous hydrochloric acid are added. To the mixture, 200 parts of a aqueous 30% formaldehyde solution are supplied in such a manner that the reaction temperature does not exceed 40° C. Once the addition has been completed, the reaction mixture is heated to 95° C and kept at this temperature for two hours until the conversion has been completed. Afterwards, at normal pressure, within one hour, the main quantity of water is azeotropically removed through distillation with aniline and then, in a thin-layer evaporator, the remaining water and aniline are removed at 150° C/1 torr and with an average residence time of three minutes. The resulting mixture of polyamines and polyamine hydrochlorides, which is crystalline at temperatures below 120° C, is cooled to room temperature, ground in of a ball mill, and 60 parts are added by using a powder screw to 400 parts of liquid water-free hydrochloric acid. The suspension is ground and mixed with an intensive mixer (Turrax TV 45) for 30 minutes at -90° C. Afterwards, the temperature is raised to 0° C, whereas hydrogen chloride removed through distillation is replaced by 400 parts by volume of phosgene.

The reaction mixture is converted to the polyisocyanate by using the autoclave described in Example 1 and under the conditions described therein. Excessive phosgene is removed through distillation, and the last phosgene residues are removed at 160° C under vacuum.

At 25° C, the 66 parts of the polyisocyanate mixture that are obtained in such a manner have a viscosity of 158 cSt and a content of NCO groups of 31.3 %.

### **Example 3**

To an aniline/aniline hydrochloride mixture of 353 parts of aniline and 20 parts of 36% hydrochloric acid, 200 parts of 30% formaldehyde are admixed in such a manner that the reaction temperature does not exceed 50° C. Once the addition has been completed, the reaction mixture is heated to 120° C, and in the process, water is azeotropically removed through distillation with aniline. The aniline is recycled, and the reaction is completed within four hours. From the polyamine base/polyamine hydrochloride mixture that is obtained after distillation by using an evaporator at 150° C and 5 torr to remove water and aniline, 60 parts are added as a 120° C molten material to 400 parts of liquid hydrogen chloride. The solid material of the resulting suspension is reduced at -90° C for 45 minutes. Afterwards, the hydrogen chloride is replaced by 400 parts of phosgene, and the reaction mixture which was heated to 0° C is transferred to the previously mentioned autoclave equipped with a reflux cooler. The autoclave is heated to 150° C, and pressure is maintained at 35 of gage pressure through expansion of

the resulting HCl. Once HCl development has been completed, excessive phosgene is removed through distillation, and the phosgene residues are removed under vacuum at 160° C and 5 torr. As a result, a polyisocyanate mixture (65 parts) with a viscosity of 241 cSt at 25° C and a NCO number of 30.6 % is obtained.

#### **Example 4**

To a mixture of 410 parts of aniline and 20 parts of 36% hydrochloric acid, while thoroughly stirring, 200 parts of 30% aqueous formaldehyde are added. The temperature is kept below 50° C. To complete the conversion, the reaction mixture is heated to 120° C, and for that purpose, water is removed through distillation together with some aniline. The aniline is recycled. After 60 minutes at 120° C, the conversion is complete. At 150° C and 5 torr, the reaction mixture is freed from water and aniline residues in a thin-layer evaporator. 60 parts of the polyamine/polyamine hydrochloride mixture obtained as a result thereof are added under intense size reduction as a molten material at a temperature of 100° C to 300 parts of liquid hydrogen chloride. After a residence time of 30 minutes at -90° C, the hydrogen chloride is replaced by 400 parts of phosgene, and in the process, the suspension is heated to 0° C. The reaction mixture is transferred to the autoclave described in Example 1 and converted at 150° C and 35 gage pressure to 66 parts of polyisocyanate, as described in Example 1. The resulting phosgene-free polyisocyanate has a NCO content of 31.7 % and a viscosity of 94 cSt at 25° C.

## Claims

1. A method for the manufacture of diisocyanates and/or polyisocyanates by means of phosgenation of the diamines and/or polyamines that were formed through condensation of formaldehyde and aniline with acidic catalysts, characterized in that:
  - a) during a first step, aniline and aqueous formaldehyde are condensed in the presence of hydrochloric acid, the reaction mixture is distilled without neutralization while separating and optionally recycling of water and/or not converted aniline, and
  - b) during a second step, the non-neutralized polyamine/polyamine hydrochloride mixture in liquid hydrogen chloride as a suspension means that was obtained during the first step is transferred to polyamine hydrochloride and, while adding liquid phosgene, the hydrochloride is converted to the polyisocyanate.
2. The method in accordance with Claim 1, characterized in that the molar ratio between aniline and hydrochloric acid is chosen between 15 to 1 and 160 to 1.
3. The use of the polyisocyanates obtained in accordance with Claim 1 as a wood glue.